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ACID-CATALYZED REARRANGEMENT OF METHYL (2aα,4aβ,6aβ,7bβ)-2,2a,5,6,6a,7b-HEXAHYDRO-2a-HYDROXY-4-METHOXYCYCLOBUT[3,4]INDENO[4,5-b]OXETE-4a(7H)-CARBOXYLATE

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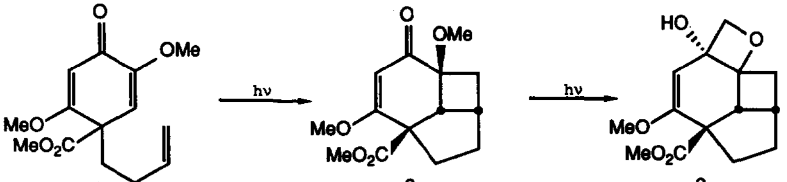
Summary: Acid-catalyzed rearrangement of 3 gives isomeric β-methoxyketone 9a, presumably via the intermediate bridgehead enone 8.

Oxetanol 3 is available in >90% isolated yield by the consecutive photoreactions of 2,5-cyclohexadien-1-one 1 and tricyclo[4.3.1.$1^{1,5}0^{7,10}$]dec-2-en-4-one 2.[1] This substance, 3, appeared to be of potential utility in

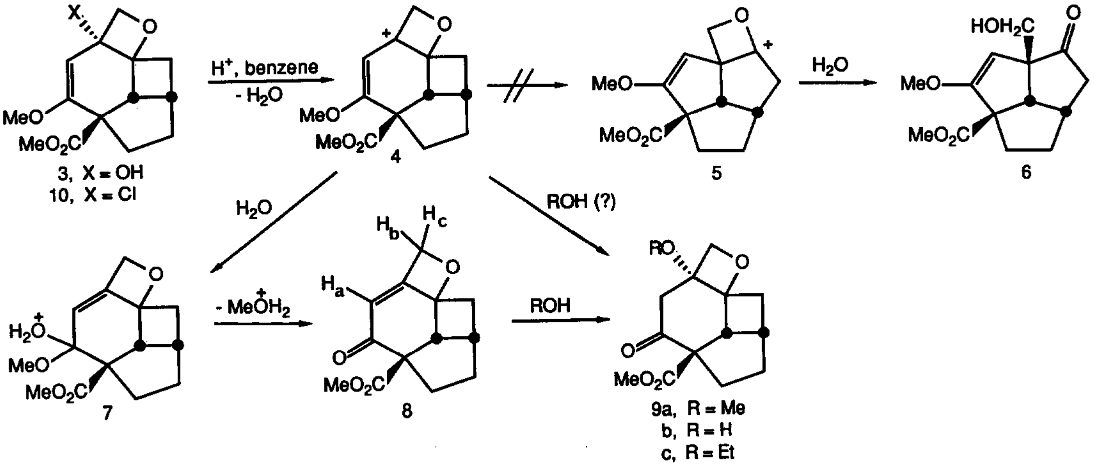


1 2 3

triquinacene ring construction;[2] a pinacol-like rearrangement[3] of 3 was expected to provide 6 or a related species. However, treatment of 3 with a catalytic amount of p-toluenesulfonic acid·hydrate (PTSA) in refluxing benzene solution followed by flash column chromatography on silica gel (hexane-ethyl acetate, 7:3) and crystallization from ethyl acetate-hexane afforded the β-methoxyketone 9a in 65% yield.[4] The structure of 9a was determined by X-ray diffraction studies.

Treatment of 3 in refluxing methanol with PTSA gave a 1:2 mixture of β-methoxyketone 9a and β-hydroxyketone 9b along with ~20% of what is tentatively assigned as enone 8.[5,6] Attempted chromatography of the reaction mixture on silica gel provided only 9a and 9b. Similar treatment of 3 in ethanol-PTSA gave 9b and 9c (1:2 mixture) along with ~15% of enone 8. Methoxyketone 9a was absent from this reaction mixture, indicating that intramolecular methyl or methoxy group transfer is not involved in the conversion of 3 to 9a. Furthermore, it was found that 9b was recovered unchanged from refluxing methanol solution in the presence of PTSA as was 9a from refluxing benzene-PTSA saturated with water.

A mechanism for the conversion of 3 to 9a-c compatible with these experimental data is shown below. The reluctance of 3 to undergo pinacol-like rearrangement, which may be a result of less than ideal bond alignment,[7] has been used to advantage in substitution processes; for example, treatment of 3 with methanesulfonyl chloride-triethylamine in methylene chloride gave bridgehead chloride 10 in excellent yield.



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References and Notes

1. Schultz, A. G.; Plummer, M.; Taveras, A. G.; Kullnig, R. K. J. Am. Chem. Soc. 1988, 110, 5547.
2. Carceller, E.; Garcia, M. L.; Moyano, A.; Serratosa, F. J. Chem. Soc., Chem. Commun. 1984, 825 and references cited therein.
3. For related acid-catalyzed rearrangements, see: (a) Cargill, R. L.; Dalton, J. R.; O'Connor, S.; Michels, D. G. Tetrahedron Lett. 1978, 4465. (b) Pirrung, M. C. J. Am. Chem. Soc. 1979, 101, 7130. (c) Pirrung, M. C. J. Am. Chem. Soc. 1981, 103, 82.
4. 9a: mp 96-98°C; ^{1}H NMR ($CDCl_3$) δ 1.69 (m, 2H), 2.08 (m, 1H), 2.45 (m, 3H), 2.88 (m, 1H), 2.98 (d, 1H, J = 15 Hz), 3.08 (d, 1H, J = 15 Hz), 3.33 (d, 1H, J = 7.8 Hz), 3.20 (s, 3H), 3.70 (s, 3H), 4.19 (d, 1H, J = 5.9 Hz), 4.59 (d, 1H, J = 5.8 Hz); ^{13}C NMR ($CDCl_3$) δ 31.01, 32.70, 32.79, 32.98, 61.21, 62.42, 62.80, 68.65, 76.97, 77.22, 88.28, 171.69, 206.02; IR (film) 2954, 1746, 1711, 1226, 1172, 1089 cm^{-1}; CIMS, m/z (relative intensity) 267 (M^+ +1, 61), 235 (100), 207 (63), 175 (47). Anal. Calcd for $C_{14}H_8O_5$: C, 63.15; H, 6.81. Found: C, 63.09; H, 6.93.
5. Enone 8: ^{1}H NMR ($CDCl_3$ in mixture with 9a and 9b) δ 6.02 (s with weak allylic coupling, H_a), 3.98 (d, J = 11 Hz, H_b weak coupling to H_a), 4.25 (d, J = 11 Hz, H_c weak coupling to H_a); GC-CIMS, m/z (relative intensity) 235 (M^+ +1, 100). For relevant ^{1}H NMR data, see: Belzner, J.; Szeimies, G. Tetrahedron Lett. 1987, 28, 3099.
6. (a) For an example of the bicyclo[4.2.0]oct-1-ene ring system, see: Skattebol, L.; Solomon, S. J. Am. Chem. Soc. 1965, 87, 4506. (b) For a review of strained bridgehead double bonds, see: Warner, P. M. Chem. Rev. 1989, 89, 1067.
7. The HO-C(2a)-C(7a)-C(7b) dihedral angle in the molecular structure of 3 (ref. 1) is 124.3°.

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